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14. ABSTRACT

The high melting point of TaC (3880°C), second amongst all known materials, along with good corrosion resistance makes TaC a potential candidate for Air Force applications. However, traditional methods of manufacturing, such as hot pressing or HIP-ing, give rise to rapid grain growth and low fracture toughness. In this work, we have utilized dynamic consolidation technique to overcome the grain growth problem, and thereby obtain stronger and more fracture resistant TaC. TaC powders of size less than 3μm, and grain size ranging from 0.5 to 1μm, were packed in double-tube steel vessels and subjected to explosive consolidation. The double-tube configuration was selected to increase pulse duration and aid plasticity induced consolidation. Almost full densification was observed near one end of the cylindrical containers, but this region also was accompanied with cracking. The hardness approached 15 GPa, similar to hardness values reported in the literature for dense TaC. In the central regions of the cylinders, the density was approximately 85% of theoretical density. However, the region was free of cracks. Post heat treatments aimed at achieving full density will be discussed in the context of improved sinterability of shock treated powders. Dynamic consolidation was also tried on nano-sized (30 - 60 nm particle size) yttria stabilized zirconia (YSZ), with the aim of obtaining nano-structured dense materials that can be further processed utilizing superplastic forming. Our results show that indeed fully dense material may be fabricated by this route, and our technique appears to overcome some of the major problems associated with consolidation of nano-materials.

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DYNAMIC CONSOLIDATION OF TaC AND NANO-YSZ POWDERS (Postprint)

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ABSTRACT

The high melting point of TaC (3880°C), second amongst all known materials, along with good corrosion resistance makes TaC a potential candidate for Air Force applications. However, traditional methods of manufacturing, such as hot pressing or HIP-ing, give rise to rapid grain growth and low fracture toughness. In this work, we have utilized dynamic consolidation technique to overcome the grain growth problem, and thereby obtain stronger and more fracture resistant TaC. TaC powders of size less than 3μm, and grain size ranging from 0.5 to 1μm, were packed in double-tube steel vessels and subjected to explosive consolidation. The double-tube configuration was selected to increase pulse duration and aid plasticity induced consolidation. Almost full densification was observed near one end of the cylindrical containers, but this region also was accompanied with cracking. The hardness approached 15 GPa, similar to hardness values reported in the literature for dense TaC. In the central regions of the cylinders, the density was approximately 85% of theoretical density. However, the region was free of cracks. Post heat treatments aimed at achieving full density will be discussed in the context of improved sinterability of shock treated powders. Dynamic consolidation was also tried on nano-sized (30 - 60 nm particle size) yttria stabilized zirconia (YSZ), with the aim of obtaining nano-structured dense materials that can be further processed utilizing superplastic forming. Our results show that indeed fully dense material may be fabricated by this route, and our technique appears to overcome some of the major problems associated with consolidation of nano-materials.

KEY WORDS: Aerospace, Fusion Technology, Nanomaterials

1. INTRODUCTION

Tantalum carbide (TaC) has a metallic luster, but may also be found as a dark to light brown powder. It is one of the monocarbides in the group IV and V transition metal, and has excellent electrical conductivity. This not only allows it to be utilized in electronic applications, but also the material can be easily wire electric discharge machined (EDM) into complex shapes, a major advantage over other ceramics. TaC can be used as an additive to WC-Co ready-to-press grade powders in order to enhance the physical properties of the sintered structure, as well as a grain growth

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inhibitor. Another purpose of the material is to form a coating on injection molds to provide low friction and wear resistance [1].

Although TaC has a hardness (~15 GPa) that is lower than other monocarbides (e.g., 25 GPa for SiC), it has the second highest melting point of known solids, 3880°C [2]. This makes TaC an excellent candidate for ultra high temperature applications, especially where erosion resistance must be maintained to very high temperatures. The material also has a ductile to brittle transition temperature (DBTT) of 1750 - 2000°C [3], allowing it to be shaped above DBTT. However, one drawback in processing is that conventional techniques such as hot isostatic pressing (HIP) or sintering above 1700°C can lead to rapid grain growth. For instance, HIP-ing of TaC for 3 hrs at 1900°C at 105 MPa pressure increased the average grain size from 22 to 57 μm [3]. In a separate instance, sintering at 2500°C for 40 minutes led to formation of voids at grain boundaries, and the grain size increased from 0.2 μm to 16 μm [4]. These large grains are detrimental to the fracture toughness and strength of the material.

In order to avoid grain growth during consolidation of TaC, our approach is to consolidate TaC and YSZ powders using shock wave processing technique [5-8]. The technique has been utilized in the past for consolidating super hard materials [5]. In the case of ceramic systems, there is some debate regarding the exact mechanism of compaction under dynamic conditions. The two primary mechanisms are believed to be local melting and bonding, and localized plastic deformation. Evidence for the former occurs in the form of local amorphous regions at particle surfaces [9, 10], while evidence for the latter is in the form of highly dislocated regions inside a particle and accompanied effects on X-ray line broadening [11, 12]. It is also well known that ceramics do plastically deform under high compressive loads, such as under an indenter. It is likely that a combination of both processes is at work during dynamic consolidation of ceramics.

There is essentially very little information in the literature on the shock consolidation of nano-size powders. Kondo and Sawai [13] were able to consolidate monocrystalline (i.e. each particle is a single crystal) diamond particles of 0.25 μm to 0.5 μm diameter, and although their final product had about 90 percent theoretical density, fracture surfaces exhibited transcrystalline fracture. This served as important evidence that interparticle bonding was strong enough to force fracture through the interior of the particles. Heat transfer calculations showed that the shock wave front was able to uniformly heat the entire diamond particle to about 1500°C, and this calculated temperature was reasoned to provide sufficient softening of the diamond to allow plastic deformation and bonding of the particles.

One important parameter in shock consolidation is the maximum pressure needed for consolidation. Figure 1 is an empirical plot [14], and shows that consolidation pressures generally scale with the hardness (in units of kgf/mm^2 = 0.01 GPa for this plot). This dependence on strength is evidence that consolidation is strongly influenced by plasticity of the particle, and the existence of DBTT for TaC is useful provided such temperatures can be realized. In Figure 1, the data for the ceramics are noteworthy. The hardness of Si_3N_4 and SiC are typically around 18 GPa and 25 GPa, respectively, and Figure 1 illustrates that they can be consolidated at about 20 to 25 GPa. Akashi *et al.* [15] were actually successful in consolidating SiC particles at pressures of 8 to 13 GPa with proper impedence matching, and they also observed some melting of the SiC particles during consolidation. In the case of superhard diamond (hardness approx. 70 GPa), Figure 1 suggests a pressure requirement around 90 to 100 GPa. On the other hand, Kondo *et al.* [13] were able to

consolidate diamond at 70 to 90 GPa, and fracture surfaces showed clear evidence of transgranular fracture, indicating excellent bonding of the small diamond particles. The hardness of TaC and YSZ are approximately 15 GPa and 12 GPa, respectively. Based on Figure 1, this would require consolidation pressures of about 20 GPa for TaC and about 18 GPa for YSZ.

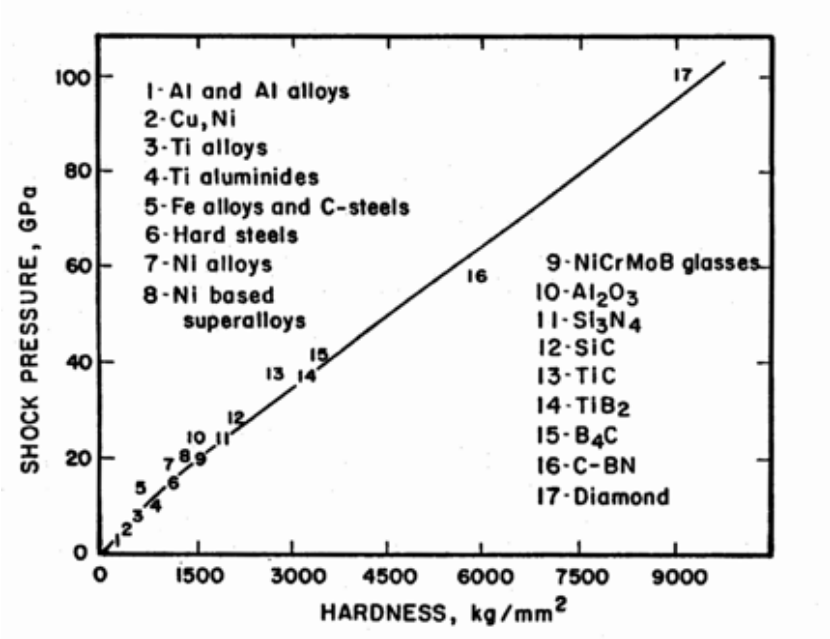

Figure 1. Engineering correlations between powder hardness and pressure required for shock consolidation [14].

In addition to achieving consolidation, it is also important to prevent cracking of the compact during the after-shock period, when tensile waves are set up in the material. The magnitude of the tensile pulse often scales with the magnitude of the initial pressure pulse, with the tensile stress as high as 0.1 times the compressive stress. Momentum traps help to minimize the shock tensile pulse, but some level of tensile stress is generally present after the primary shock pulse has passed through. The tensile wave is of special concern for ceramic materials, because of their low fracture toughness. That is why it is important to keep pressure pulses to a minimum, while still sufficient to consolidate the particles in the first place. Particle size also plays an important role in this regard. Large particles possess larger defect sizes, and are therefore more prone to cracking; $\sigma_{fracture} \sim K_{IC}/\sqrt{\pi a}$, where 'a' is the crack radius that scales with particle size, and K_{IC} is the fracture toughness of the material; a typical value of 4 - 6 MPa $\sqrt{m}$ for structural ceramics like SiC and Si_3N_4. Thus, coarse particles tend to provide larger defect sizes, and this has been established in a number of systems, such as diamond [16]. Therefore, nanoparticles are attractive in this regard, and the work of Kondo *et al.* [13] demonstrates success with diamond particles. On the other hand, finer particles have higher friction, and green bodies tend to have higher defect population.

In this paper we use a double tube steel container and ammonium nitrate/fuel oil (ANFO) explosive to perform the consolidation of TaC and YSZ powders. Heat-treatment and microstructural characterization were conducted on the after-shock samples. The Vickers' hardness was measured for various experimental conditions.

We hope the results of the investigation can shed an insight on how to obtain an optimum dynamic consolidation route for TaC and nano YSZ powders.

2. EXPERIMENTAL

The TaC powder with purity of 100% was received from Inframat Advanced Materials, LLC. The average size of particles is less than 3 μm, with a majority being in the range 0.5 to 1 μm. The nano powder of yttria stabilized zirconia (YSZ) was also provided by this company. The purity was 99.95+%. The average YSZ particle size lay within the range of 30 - 60 nm.

The consolidation of the powders was conducted using double-wall cylindrical cans, in the arrangement shown schematically in Figure 2. This method is favored in place of a flyer plate assembly because it has the potential to provide reasonably sized samples that can be bend-tested. Also, the double-tube geometry provides a stronger pressure pulse of longer duration than a single-tube geometry, thereby aiding powder consolidation [7, 14].

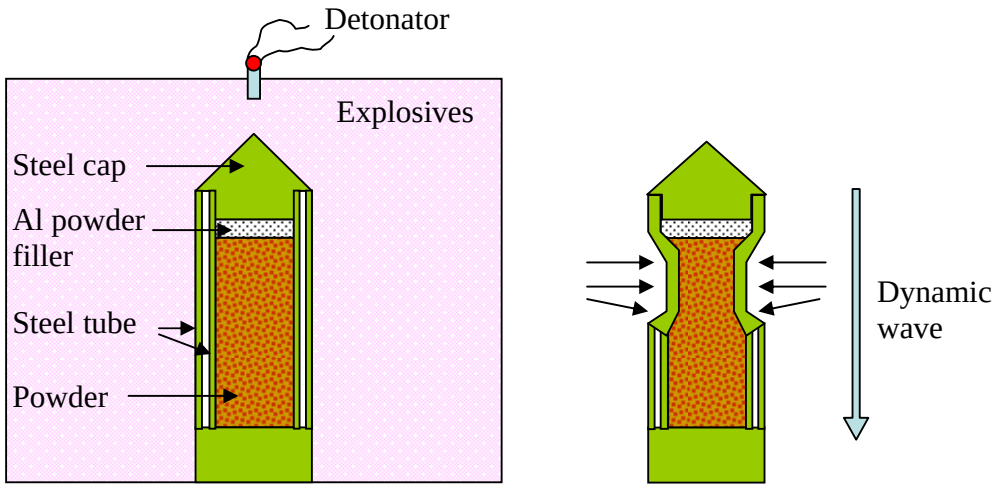

Figure 2. Schematic of cylindrical geometry for shock wave consolidation of powders.

The packing density is an important parameter in explosive consolidation, and previous research indicates that best consolidation is obtained when the packing density lies between 65% and 70% of full theoretical density. In an attempt to achieve this value, we employed a repetitive route as follows: add powders in small quantities, evacuate the can from the bottom through a pre-drilled hole, and press the powders to higher density using a punch. In some cases, the powders were heated to 250°C immediately before packing to drive off adsorbed moisture on the particles.

In the case of the micron sized TaC powders, we were successful in obtaining fairly high packing density, namely 60 - 65% of the theoretical density. Although the highest density for packing of single size spherical particles is 74%, the results from experiment and computer simulation indicate that it is difficult to obtain density above 60 - 64% [17]. The packing density of *nano* YSZ powders was, however, very low: only about 40 - 45%. This powder was initially very fluffy, and friction appeared to drive the packing pressure higher compared to the micron sized powders.

The explosive type and quantity were selected to obtain a pressure of about 20 GPa in the powder region. Higher pressures were avoided in order to minimize cracking of the billet arising from reflected tensile waves. Following shock wave

consolidation, the cylindrical billets were sliced into approximately 5mm thick disks along the length of the sample using a slow diamond saw cutter. The disks were mounted and polished for optical and SEM microstructure observations. The steel shell around the cut disks was removed for heat-treatment purpose. The sectioned specimens were heated at 1100°C for 6 hrs and 24 hrs under a low argon flow atmosphere. The hardness values for various samples were measured using a HVS-1000 digital micro hardness tester.

3. RESULTS

Figure 3 shows macroscopic views of the billets before and after consolidation. The caving in of the double-wall region corresponds to the densification of the billets. The powders were nearly fully dense at the bottom region of the billets (see Figure 4).

Figure 3. Photographs of the billets before and after consolidation.

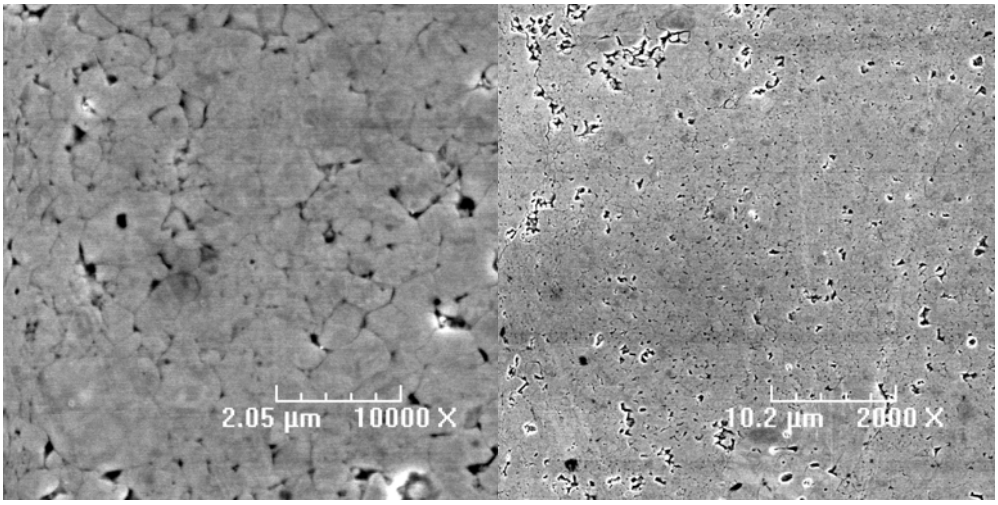

Figure 4. Microstructure of TaC near the bottom of the can. The consolidation here is good. However, there were radial and circumferential cracks.

Note that individual grains are visible, but the porosity is fairly small. The hardness in this region averaged about 14.5 GPa, which is in good agreement with published data for fully dense TaC (15 ± 0.5 GPa). Unfortunately, this bottom region also contained cracks. This type of behavior was observed in most of the billets, and

suggests that our momentum trap was not very effective in minimizing tensile shock pulse. The fracture toughness of the sample in this region, as measured from indentations tests, was 4.8 MPa√m. For comparison, the fracture toughness of structural ceramics such as SiC and Si_3N_4 lie in the range of 4 to 6 MPa√m, although higher values have also been obtained for SiC.

At around the half-length of the consolidated billets, the density measured using the Archimedes technique was 11.6 g/cm^3 compared to a theoretical density (TD) of 13.9 g/cm^3 for the powders, as quoted by the powder manufacturer (Inframat Advanced Materials). The density values at mid-length translate to a compaction of approximately 83% theoretical density. Hardness measurement in this region gave a hardness of only 4.8 GPa, considerably lower than the value measured at the bottom (~15 GPa) of the billet. This lowering of hardness is consistent with the lower relative density of the central region compared to the bottom of the billet. However, this central region also did not reveal any crack, and three bend bars have been successfully machined from the billets.

The absence of cracks in the mid-length region is considered very encouraging, especially because the density is already 83% of theoretical density. Thus, one may consider heat treatment and/or HIP-ing of the 83% dense material to obtain fully dense TaC. One advantage is possible plasticity of the TaC produced by shock wave consolidation, which would thereby enhance creep and sintering of the TaC powders. Representative TEM samples have been prepared from the consolidated billets as well as the as-received powder. Results of dislocation analysis will be reported in the near future.

We have conducted preliminary heat treatment in argon atmosphere at a relatively low temperature of 1373 K (1100°C), which is well below half the melting point of 4153 K (3880°C). In this regard, it may be noted that diffusion effects become dominant at homologous temperature ($T_H = T/T_{MP}$, in K) above 0.5, whereas 1100°C corresponds to a T_H of only 0.33. Following heat treatment, the overall density did not change by any significant amount from the initial TD of 83%. However, a thin strip of high reflectivity with a golden TiN-color could be observed around the periphery of the sample. SEM observations indicated that this rim region was significantly denser than the inner 83% region.

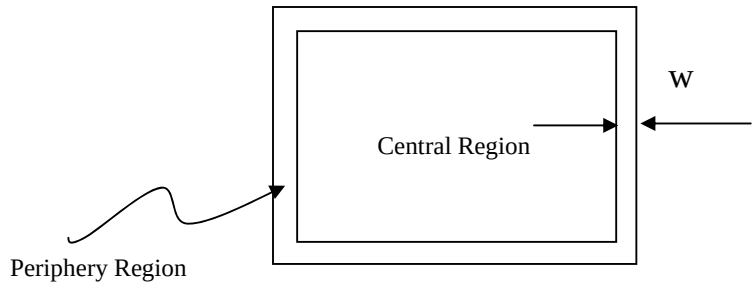

Figure 5. Sketch illustrating the cross section of the heat treated sample. The thickness of the periphery region is designated as 'w'. Heat treatment was conducted at 1100°C. The width, *w*, was 50 μm and 130 μm for the 6 hr and 24 hr heat treatments, respectively.

The sketch in Figure 5 illustrates the denser region of the heat-treated samples. The width, *W*, was 50 μm for the sample heat treated for 6 hours, and approximately 130 μm for the 24 hr sample. The increased width with heat treatment time is consistent with diffusion kinetics. Additional data is needed before we can estimate

activation energy from the rate of zone growth. More importantly, the diffusion at such a low temperature is encouraging and may point to increased diffusion in the shock-consolidated billet.

Hardness measured for the 24 hr heat-treated sample revealed a hardness of approximately 11 GPa in the rim region and 6.4 GPa in the interior. Note that the hardness did increase by about 33% even in the interior region, suggesting that even 1100°C is sufficient to provide some density increase. In addition, the significant increase in hardness in the outer region is consistent with high reflectivity of the periphery region, as well as low defect density observed in the SEM. The hardness of 11 GPa represents a 130% increase compared to the as-consolidated billet, and may be adequate for certain applications. Additional heat treatments at higher temperatures are planned, and the hardness data as well as strengths of heat treated bend bars from the mid-length region of the billets will be reported in the near future. Further, one important advantage of the surface related sintering is that it can serve as a good method to close off the inside from the surface, thereby allowing HIP-ing at high temperatures and pressures. As indicated earlier, success with heat treatments and HIP-ing may provide a pathway to fine grain-size TaC, without the problem of cracking that occurs in the bottom regions of the billets.

At the end of this section, we would also like to report on the characterization of the YSZ billet. This billet started out with a poor packing density of 40 - 45%. As indicated earlier, the fluffiness and friction of the powders likely contributed to this problem. A consequence of this problem was that the central region of the billet showed very little consolidation. However, the bottom region did consolidate well, except for a few radial cracks. Figure 6 is a metallographic section of the bottom region of this billet. The micrograph illustrates a very smooth surface without any features.

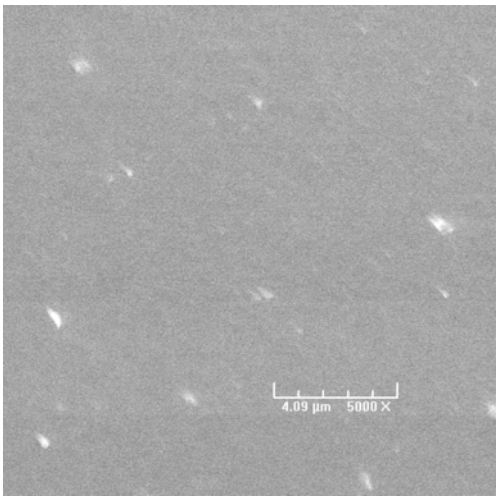

Figure 6. Microstructure of YSZ sample, showing no features. The micrograph is taken from the bottom region of the consolidated billet.

The density of this sample has not been measured. However, the fracture surface revealed transgranular fracture that spanned across many particle sizes. Figure 7 shows micrograph of the fracture surface at low magnification. Cleavage markings may be observed. Hardness measurements showed a hardness of 9.7 GPa, which is also comparable to reported hardness of fully dense zirconia (12 GPa) [2].

This result is also quite encouraging, and may prove to be another success of the dynamic consolidation technique.

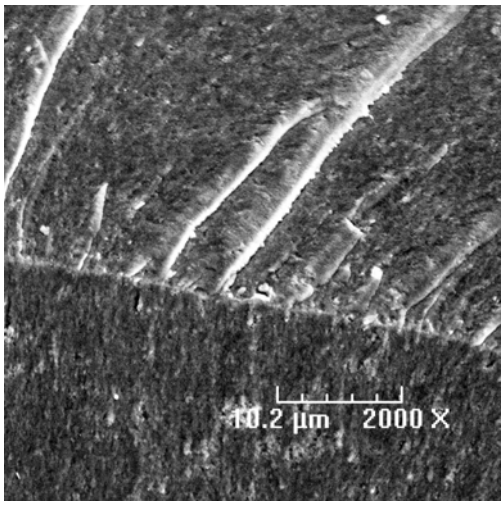

Figure 7. Fracture surface of the YSZ sample. The surface exhibits typical cleavage type fracture. The line going from left to right in the central region of the photograph corresponds to a major shift in surface normal.

4. SUMMARY

The following summarizes our observations:

(1) Dynamic consolidation trials of TaC powders (from Inframat) indicate promise, and confirm that the double-tube method is a good approach for consolidating TaC powders.
(2) Cracking has been absent in the mid-length of the billets, although the density there is only 83% of theoretical density. Heat treatments in argon at 1100°C suggest that sintering may be active at this low temperature around the periphery of the sample. The hardness there reached approximately 11 GPa, comparable to a hardness of 15 GPa of fully dense TaC.
(3) The consolidation trial with YSZ was quite successful, in spite of a low tap density. The hardness of 9.7 GPa HV in the bottom region was comparable to literature values of 12 GPa. Fracture surfaces revealed transgranular fracture that spanned many individual YSZ particles, and confirmed consolidation of the nano YSZ.

5. ACKNOWLEDGEMENT

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